Terahertz Spectroscopic Characterization of Paper

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***Abstract*—THz-TDS of paper was performed. The real and imaginary indices depended on frequency, orientation, type of paper, and moisture content. The attenuation coefficient depended quadratically on frequency. Moisture content dependence was consistent with the complex permittivity of liquid water.**

I. Introduction And Background

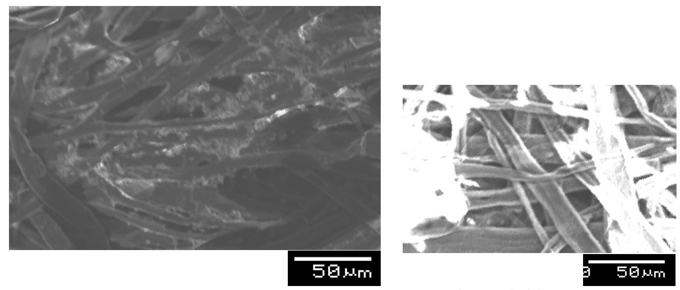
DETECTION and observation of objects through paper has been a central subject of terahertz wave applications. Terahertz waves can pass through paper because of low scattering and low absorption of terahertz waves in paper. The spectroscopic properties of paper, however, have not been fully characterized, which is required for extending the application of terahertz waves in this field. Previously, watermarks in currency papers have been observed by terahertz imaging [1]. Water content [2,3], composition [4], and birefringence [5] of paper have already been studied by terahertz spectroscopy. In this study, we have analyzed and interpreted the spectroscopic characterization of paper properties, such as paper type, moisture content, and orientation, based on the Lorentz-Lorenz and the Clausius-Mosotti relations.

II. Results

We performed terahertz time-domain spectroscopic (THz-TDS) measurements of paper. Attenuation coefficient and refractive index spectra of paper were obtained. Samples were stacked sheets of white copy paper and weighing paper. TEM images of the sample papers are shown in fig. 1. Higher orientation of cellulose fibers in copy paper is seen from the images. It is also seen that additives, which are mainly composed of chalk ($CaCO_3$), exist in copy paper. Examples of time-domain data and spectra obtained are shown in fig. 2. Since paper, mainly composed of cellulose fibers, is known to adsorb ambient moisture, and the moisture content depends on the humidity, all the measurements were performed under an ambient humidity of 56%, which leaded to oscillations in the time-domain data and artifacts in the observed spectra as oscillatory features due to water vapor absorption of terahertz waves.

Examples of attenuation coefficients obtained are shown in fig. 3. The attenuation spectra were found to depend quadratically on frequency in the frequency range of 0.2 to 1.0 THz. Loss of terahertz waves due to scattering by the cellulose fibers were estimated using a model of independent scattering by cylindrical cellulose fibers [6], which should be an overestimate of scattering because the fibers are much thinner than the terahertz wave wavelength. The calculation shows that the contribution of scattering to the observed attenuation is negligible, and the observed attenuation is mostly attributed to absorption of terahertz waves in the paper.

Obtained sample dependence and orientation dependence of refractive indices are summarized as follows. All the data showed anomalous dispersion between 0.2 and 1.0 THz. The index for THz waves polarized in the cellulose fiber orientation is higher than that of orthogonal polarization, and the difference is large for copy paper (0.021), and small for weighing paper



(a) Copy paper (b) Weighing paper

Fig. 1. TEM images of copy paper and weighing paper. The main orientation direction of fibers is horizontal in these images.

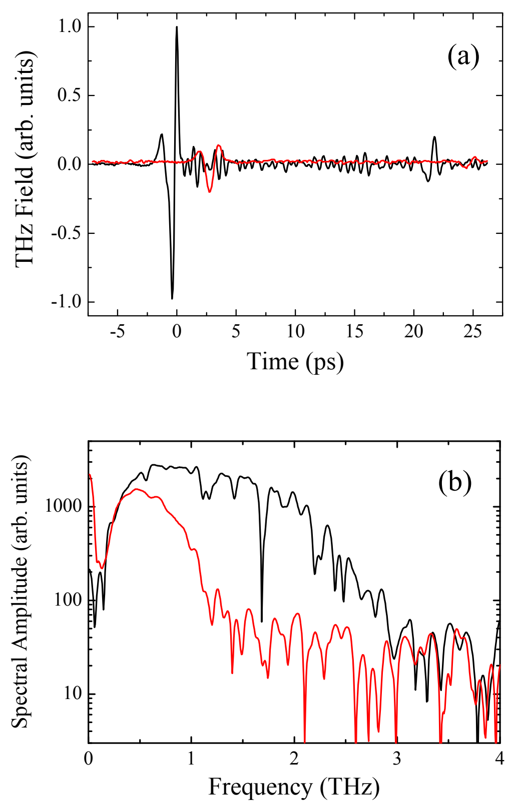


Fig. 2. An example of (a) THz waveforms and (b) spectra obtained by the THz-TDS measurements. Red lines are data of THz waves transmitted through a sample, and black lines are reference obtained without a sample.

(0.002). This difference is attributed to the difference in degree of orientation of cellulose fibers in the sample papers [5]. Copy paper has a larger index by about 0.02 than weighing paper throughout the observed frequency range. Copy paper has a higher density, and the analysis based on Lorentz-Lorenz relation lead to overestimate of the index of copy paper, which shows non-negligible effects of chalk additive, which has density much higher than cellulose, to the THz properties of paper.

Effects of moisture content in paper were studied by comparing the spectra of copy paper kept under ambient humidity and that dried using a hair dryer for a several minutes. The dried paper was found to have a smaller refractive index and attenuation coefficient. In fig. 4 are shown the spectra of refractive index and attenuation coefficient. Using the Clausius-Mossotti relation and the liquid water permittivity spectrum [7], it was found that the observed refractive index and attenuation coefficient spectrum of undried paper are consistent with a model system composed of dried paper and 1.7 wt% liquid water. The calculated spectra are also plotted in the figures. It was reported that water hydrated to disaccharide has less terahertz absorption than liquid water [8]. Diffusion of water adsorbed in cellulose fibers has been studied with NMR [9]. The results suggested that the diffusion constant is larger for high water content, and that there are immobile water, water molecules directly hydrated to the cellulose fibers, and mobile water, which is loosely combined. Under the relative humidity of 56% in the present study, the equilibrium water content is estimated to be about 8%, and the Clausius-Mosotti estimation of 1.7% water content, as described above, suggests that the drying by a hair dryer only partly reduced mobile hydrated water.

III. SUMMARY

We have performed THz-TDS studies of papers (copy paper and weighing paper), and obtained the dependence of terahertz attenuation and refractive index spectra on paper density, cellulose fiber orientation, and water content. The results were explained using the Lorentz-Lorenz and the Clausius-Mossotti relations. The water content dependence was consistent with liquid water permittivity.

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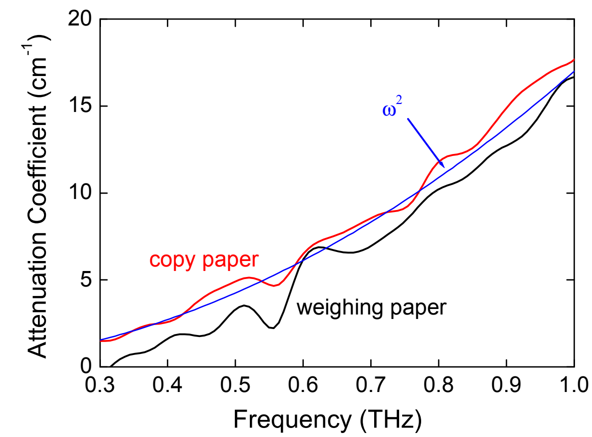

Fig. 3. Terahertz attenuation coefficient of two types of paper, averaged over paper orientation. Oscillatory features are artifacts due to water vapor absorption. Quadratic function is shown in blue line as a guide.

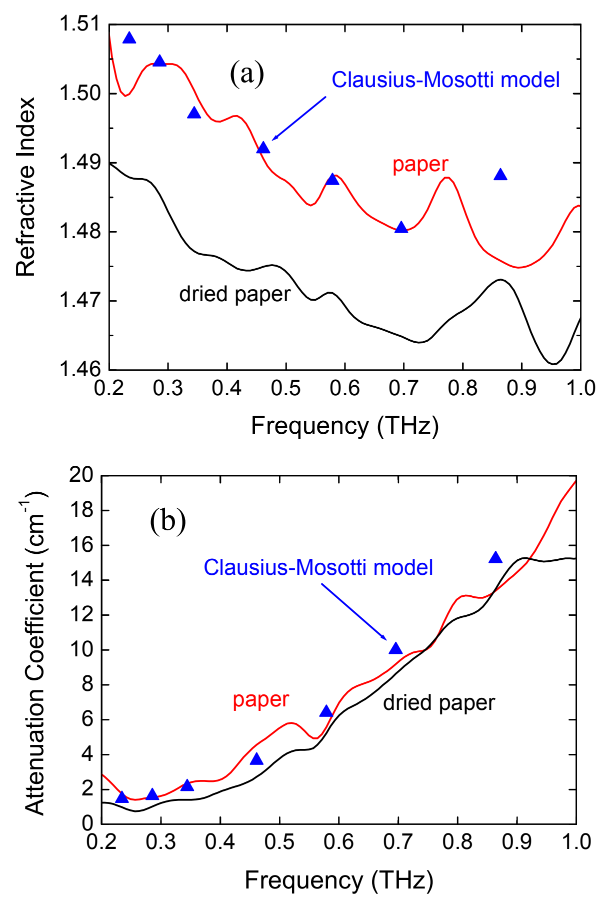

Fig. 4. Spectra of (a) refractive index and (b) attenuation coefficient of copy paper under ambient humidity and dried copy paper, compared with calculation using the Clausius-Mosotti relation. Oscillatory features are artifacts due to water vapor absorption.